Effect of UV/Ozone Treatment on Surface Tension and Adhesion in Electronic Packaging

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***Abstract*—Surface tension of material surfaces and interfaces is an important parameter that affects wetting and adhesion. Surface tension can be divided into three components: Lifshitz–van der Waals component, acid component, and base component. In this study, the three-liquid-probe method was used to investigate the surface tension and its three components of various surfaces of electronic packaging materials: benzocyclobutene (BCB) passivation, FR-4 board, polyimide board, and alumina board. When UV/ozone was employed to treat the surfaces, the surface tension increased, and the base component increased the most. The change in surface tension due to UV/O_3 treatment decayed with time after the treatment. The difference in surface tension between untreated and treated surface became smaller with the increase of time after UV/O_3 treatment. Different substrates showed different rate of decay in surface tension change. Among the surfaces studied, BCB passivation showed the fastest decay after treatment, while alumina showed the slowest decay. The contact angles of several liquid underfill materials on BCB passivation and their surface tension before and after curing were also measured. It was found that the wetting was not the controlling factor in adhesion of the system investigated.**

***Index Terms*—Adhesion, alumina, BCB passivation, contact angle, surface tension, underfill, UV/O_3 treatment.**

I. Introduction

MANY different materials are used in electronic packaging today, and the adhesion at the interfaces between the different materials is critical to the reliability of the package. In flip chip assembly, delamination between die and underfill encapsulant is still a major concern for yield loss and reliability [1], [2]. Delamination can be caused by the thermal stress due to mismatch in the coefficient of thermal expansion of adjacent materials. The problem of delamination is particularly common when the assembly is subjected to thermal cycling in a high humidity environment. There are many reasons for delamination such as: low adhesion due to incompatible surfaces, contamination, and void formation during curing. Delamination at the underfill/die or underfill/substrate interface of flip-chip package can lead to cracking of the solder joint interconnection [3]. Delamination in plastic package can result in metal line deformation, passivation crack, wirebond shear, and dielectric and epoxy molding compound crack [1], [4], [5]. In addition to thermal stress, moisture can also cause delamination. Moisture can diffuse into a plastic package. When the package becomes saturated with moisture, water tends to aggregate at interface due to osmotic pressure, and thus separation at interface can occur at high temperature and humidity [6]. Water-borne contaminants can enter the package through the delaminated area, then be trapped in the gap, and cause corrosion of metal pad, joint, and metal line.

Surface tension plays an important role in interfacial adhesion. Wetting, spontaneous spreading of a liquid on a solid surface, is an important step in the adhesion of polymer adhesives. Wetting can increase total contact area between the liquid and the solid, reduce the voids and defects. The contact angle (θ) of a liquid on a solid is a quantitative measurement of wetting. The smaller contact angle, the better wetting. Contact angle is directly related to the surface tension of the solid surface (γ_{sv}), the liquid surface (γ_{lv}), and the interface between solid and liquid (γ_{sl}). Their relationship is given by Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\mathrm{Cos}(\theta). \tag{1}$$

It was proposed that the surface tension is composed of three components [7], [8]: the Lifshitz–van der Waals component (γ^{LW}) including electromagnetic interaction, oscillation temporary dipoles interaction, and permanent and induced dipoles interaction; the Lewis acid component (γ^{+}); and the Lewis base component (γ^{-}). Their relationship is given by the following equation:

$$\gamma = \gamma^{LW} + 2(\gamma^{+}\gamma^{-})^{1/2}. \tag{2}$$

Thermodynamic work of adhesion (W_a, also called physical adhesion) is the reversible work required to separate a unit area of two contacting phases. It is composed of LW component (W^{LW}) and acid-base component (W^{AB}), and it is directly related to the surface tension. The nongeometric combining rule was proposed [9]

$$W_A = W^{LW} + W^{AB} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{3}$$

$$W^{LW} = 2(\gamma_1^{LW}\gamma_2^{LW})^{1/2} \tag{4}$$

$$W^{AB} = 2(\gamma_1^{+}\gamma_2^{-})^{1/2} + 2(\gamma_1^{-}\gamma_2^{+})^{1/2} \tag{5}$$

where γ_1 and γ_2 are surface tension of component 1 and component 2, respectively, and γ_{12} is the surface tension of the interface between the two components. It was suggested that surface modification can alter the acid-base component rather than LW component, and thus the work of adhesion can be enhanced by

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surface modification through increasing the acid-base interaction [10].

The three-liquid-probe was proposed to measure the surface tension and its three components of any solid surface [9], [11], [12]. Water, ethylene glycol can be used as two polar liquids, and diiodomethane is frequently used as the apolar liquid. The surface tension and its three components of the probe liquids are shown in Table I.

The work of adhesion between a solid and a liquid can also be expressed by the following equation, deduced from (1) and (3)

$$W_A = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} = \gamma_{lv}(1 + \mathrm{Cos}(\theta)). \tag{6}$$

Thus, the three components of surface tension of any solid (γ_s) can be obtained by measuring the contact angles (θ_1, θ_2, θ_3) of the three liquids (with known surface of γ_1, γ_2, and γ_3) on the solid surface and solving the following three equations deduced from (3)–(6) [13]:

$$\gamma_1(1 + \mathrm{Cos}(\theta_1)) = 2(\gamma_1^{LW}\gamma_s^{LW})^{1/2} + 2(\gamma_1^{+}\gamma_s^{-})^{1/2} + 2(\gamma_1^{-}\gamma_s^{+})^{1/2} \tag{7}$$

$$\gamma_2(1 + \cos(\theta_2)) = 2(\gamma_2^{LW}\gamma_s^{LW})^{1/2} + 2(\gamma_2^{+}\gamma_s^{-})^{1/2} + 2(\gamma_2^{-}\gamma_s^{+})^{1/2} \tag{8}$$

$$\gamma_3(1 + \cos(\theta_3)) = 2(\gamma_3^{LW}\gamma_s^{LW})^{1/2} + 2(\gamma_3^{+}\gamma_s^{-})^{1/2} + 2(\gamma_3^{-}\gamma_s^{+})^{1/2}. \tag{9}$$

Many factors, such as surface cleanness, surface treatment, and surface uniformity, affect surface tension and contact angle measurement. UV/ozone is commonly used to clean the substrate surface. In this study, the surface tension and its three components of various substrates used in electronic packaging before and after UV/ozone treatment are measured through three-liquid-probe. The surface property is also characterized by contact angle measurement at different time after UV/ozone treatment. The effect of surface treatment on adhesion with epoxy underfill is also investigated. In addition, thermodynamic work of adhesion of underfill with BCB passivation is compared with adhesion strength of underfill on BCB passivation.

TABLE I
SURFACE TENSION OF THREE PROBE LIQUIDS

Liquid	γ mJ/m^2	γ^{LW} mJ/m^2	γ^{+} mJ/m^2	γ^{-} mJ/m^2
CH_2I_2	50.8	50.8	0	0
H_2O	72.8	21.8	25.5	25.5
HOC_2H_4OH	47.9	29.0	1.9	47.0

TABLE II
CONTACT ANGLES (IN DEGREE) OF THREE LIQUIDS ON SUBSTRATES

Substrate	H_2O	HOC_2H_4OH	CH_2I_2
Before UV/O$_3$ treatment			
FR-4	77	61	45
Polyimide	111	73	79
BCB	88	67	59
Alumina	76	50	45
After UV/O$_3$ treatment			
FR-4	23	4	39
Polyimide	0	0	49
BCB	35	33	64
Alumina	8	0	26

TABLE III
SURFACE TENSION OF DIFFERENT SUBSTRATES

Substrate	γ mJ/m^2	γ^{LW} mJ/m^2	γ^{+} mJ/m^2	γ^{-} mJ/m^2
Before UV/O$_3$ treatment				
FR-4	38.9	37.0	0.08	11.9
Polyimide	18.9	17.8	1.62	0.20
BCB	29.9	29.3	0.02	5.43
Alumina	39.1	37.0	0.12	8.91
After UV/O$_3$ treatment				
FR-4	47.6	40.2	0.25	55.7
Polyimide	-	34.9	-	-
BCB	40.0	26.1	0.86	56.1
Alumina	-	45.9	-	-

II. EXPERIMENTAL

A. Materials

Deionized water, diiodomethane (99%, from Aldrich), and ethylene glycol (99+%, from Aldrich) were used as standard liquids for contact angle measurement. Benzocyclobutene (BCB) passivated silicon die was supplied by Dow Chemical. The FR-4 board was from Stanley Circuits. The polyimide board was supplied by National Semiconductor Corp.

An epoxy underfill was prepared with a cycloaliphatic epoxy resin, an acid anhydride as hardener, and a latent catalyst. Coupling agent (CA) of 1.5% weight of the underfill was added into the underfill, and dispersed homogeneously by stirring.

B. Contact Angle Measurement

The substrates were cleaned according to standard procedure [14]. The steps were as follows: 5 min soak in terpene; 5 min soak in terpene during ultrasonic cleaning; 5 min soak in isopropyl alcohol; 5 min soak in isopropyl alcohol during ultrasonic cleaning; three rinses in deionized water for 2 min each time; dry in a vacuum oven at 120 °C for 30 min with pressure below 30 mmHg. UV/ozone treatment of the surfaces was performed at 50 °C for 5 min in an UV & ozone dry stripper (Samco, Model UV-1). A goniometer (Model 102-00, from Rame-hart, Inc.) was used to measure the contact angle. A substrate was placed on the sample stage of the goniometer, and a micro syringe was used to deposit a liquid drop of 2–3 μl on the surface of the substrate. The steady-state contact angle

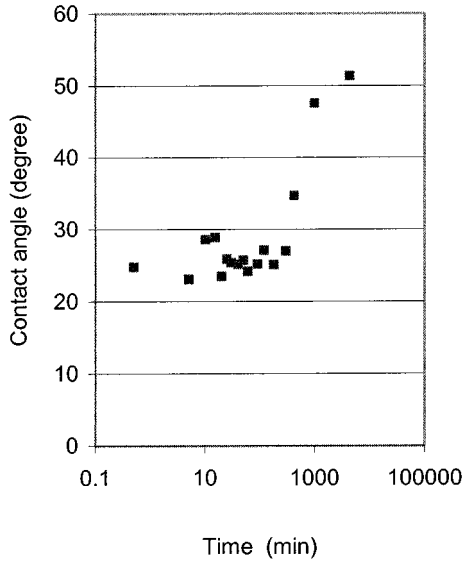

Fig. 1. Contact angle of water on UV/O_3 treated FR-4 board versus time after treatment.

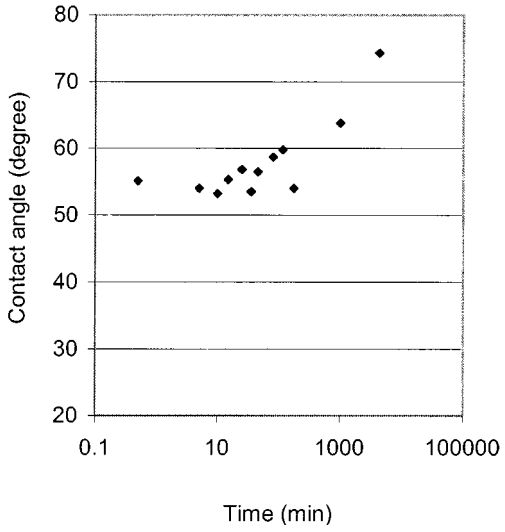

Fig. 2. Contact angle of CH_2I_2 on UV/O_3 treated polyimide board versus time after treatment.

was recorded within 30 s after the formation of the sessile drop. Five readings were taken, and the average was reported unless otherwise indicated.

C. Surface Tension Measured by Pendant Drop Method

The pendant drop method was used to determine the surface tension of uncured underfill materials with or without coupling agents. A stable pendant drop of underfill material was created by dispensing the underfill through a polytetrafluroethylene needle (18 G) at room temperature. The profile of the pendant drop was captured by the imaging system of the goniometer, and analyzed to give the surface tension. Ten readings were obtained for each sample, and the average was reported.

D. Die Shear Sample Preparation and Test

The adhesion strength of underfill with passivation was measured through die shear test. Underfill materials with different coupling agents were used to prepare die shear samples. Small BCB passivated die ($2mm \times 2mm$) was dipped into a thin liquid film of the underfill to coat a uniform thin layer (with glass beads with a diameter of 75 μm as spacers), and then placed on a large piece of BCB passivated silicon wafer (2 cm $\times$ 2 cm). The die shear samples were placed in an oven at 250 °C for 30 min to cure the underfill. Die shear test was performed 12 h after the curing of the underfill. In order to test adhesion of underfill with alumina, SiO_2 passivated dies (2 mm $\times$ 2 mm) and large alumina substrates were used to prepare the die shear samples.

III. Results and Discussion

A. Determination of the Three Components of Surface Tension of Different Substrates

Table II shows the contact angles of water, ethylene glycol, and diiodomethane on FR-4 board, polyimide board, BCB passivation, and alumina board. The contact angles of water, ethylene glycol, and diiodomethane on UV/O_3 treated surfaces were measured immediately after the treatment and are also shown in Table II. The contact angles of water and ethylene glycol on all of the substrates decreased significantly after the UV/ozone treatment. Both water and ethylene glycol showed a contact angle of 0° on UV/ozone treated polyimide board. Ethylene glycol showed a zero contact angle on treated alumina board too. This suggested that the substrate became more hydrophilic after UV/ozone treatment. The contact angles of diiodomethane on treated FR-4, polyimide, and alumna also decreased. The contact angle of diiodomethane on BCB passivation increased slightly after the UV/ozone treatment.

From equations (7)–(9), the total surface tension and their three components were calculated and are listed in Table III. The surface tension of FR-4, polyimide board, BCB passivation, and alumina before UV/O_3 treatment are 38.9, 18.9, 30.0, and 39.1 mJ/m^2, respectively. Among the three components of surface tension, the LW component contributes the most to the total surface tension.

The Young's equation is not valid for system showing zero contact angle. Since the contact angles of water and ethylene glycol on treated polyimide surface were zero, the acid and base components of surface tension of polyimide board after UV/O_3 treatment could not be calculated, and only the LW component was calculated through (7). Similarly, only LW component was calculated for UV/O_3 treated alumina board, due to zero contact angle of ethylene glycol on the treated surface. The surface tension and their three components of UV/O_3 treated FR-4 and BCB were calculated and are listed in Table III. The surface tension value of all tested substrates increased after UV/O_3 treatment. The LW components of surface tension of FR-4, polyimide and alumina also increased significantly. The base components of UV/ozone treated FR-4 and BCB passivation are much higher than those of untreated surfaces.

The UV/ozone treatment can remove the hydrocarbon contamination on the substrate surface. Since hydrocarbons have low surface energy, the removal of hydrocarbons from the surface leads to an increase in the surface tension. In addition to the removal of hydrocarbon contaminant from the surface, oxide bonds can form on the substrate surface during UV/O_3 treat-

ment, which leads the surface to be more hydrophilic and show higher surface tension. The oxygen atom is a Lewis base. More Lewis base sites on the surface lead to a higher base component of the surface tension.

Compared with other substrates, BCB passivation showed some different behavior. After UV/ozone treatment, the contact angle of diiodomethane increased, and the LW component decreased slightly. This is possibly due to its structure composed mainly of hydrogen and carbon elements.

B. Contact Angle on UV/O_3 Treated Surface as a Function of Time After Treatment

The surface property was changed during the UV/ozone treatment. However, this change in surface property was not stable. The contact angle measurement on the UV/O_3 treated surface versus time after treatment showed that the change in surface tension due to UV/O_3 treatment decayed with time. Fig. 1 shows the contact angle of water on UV/ozone treated FR-4 board versus time elapsed after the treatment. In this experiment only one sessile drop was formed each time, and the readings of both right and left side contact angles were averaged and plotted. The contact angle of water on the treated FR-4 board did not show obvious change during the initial 100 min after the UV/O_3 treatment. The contact angle of water on the treated FR-4 board increased from around 25° to more than 50° when 1000 min passed after the UV/O_3 treatment.

The contact angle of water on UV/O_3 treated polyimide board was zero, while the contact angle of diiodomethane decreased significantly but not to zero. Thus, diiodomethane instead of water was used to monitor the decay of surface tension change after UV/O_3 treatment. The results are shown in Fig. 2. In the first 2 hours after the treatment, contact angle on the treated surface remained around 55°. Significant increase in contact angle occurred around 10 hours after the treatment. Seventy hours after the treatment, the contact angle approached to that before UV/O_3 treatment. Among all the substrates being tested, BCB passivation showed the fastest decay in surface tension change versus time after UV/O_3 treatment. Fig. 3 shows contact angle of water on the treated BCB passivated silicon wafer versus time after the UV/O_3 treatment. Five minutes after the treatment, the contact angle of water on the treated BCB showed a rapid increase. In less than two hours, the contact angle of water on treated BCB returned to the original value before UV/O_3 treatment (from 30° to 90°).

Among the substrates being tested, alumina board showed the slowest change in the contact angle versus time after UV/O_3 treatment. Fig. 4 shows the contact angle of water on UV/O_3 treated alumina versus time after the treatment. As was mentioned earlier, the contact angle decreased dramatically due to the UV/O_3 treatment, from 76° before treatment to 10° after treatment. The contact angle of water on the treated alumina remained around this low value for up to 2 h. Seven hours after the treatment, the contact angle started to increase. However, it did not return to the original value before treatment. Ten days after the treatment, the contact angle of water on the treated alumina board was around 60°, significantly lower than original value of 76°. In fact, the color of the surface was changed from white to yellow during the UV/O_3 treatment. The yellow color on the

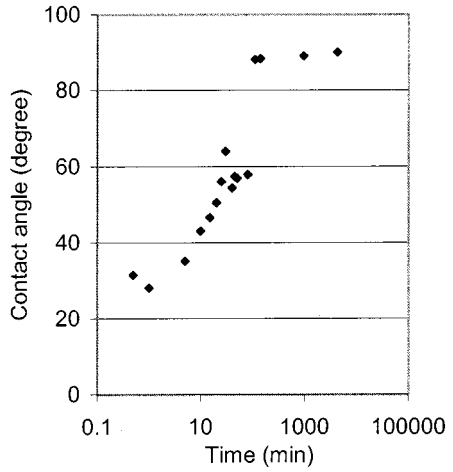

Fig. 3. Contact angle of water on UV/O_3 treated BCB versus time after treatment.

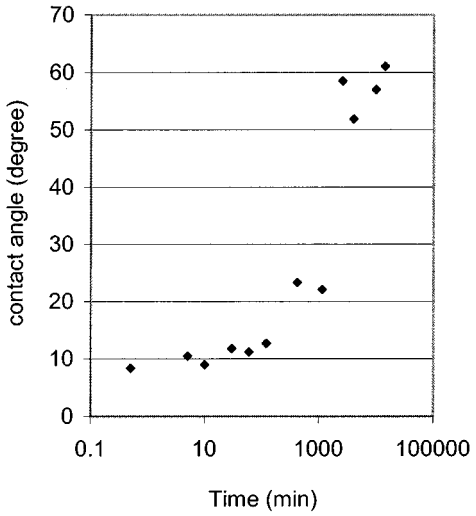

Fig. 4. Contact angle of water on UV/O_3 treated alumina versus time after treatment.

alumina surface did not show any decay as the time elapsed after the treatment.

The decay of the contact angle change versus time after UV/O_3 treatment is due to several reasons. The most important reason is the re-contamination of the surface by hydrocarbons in air. Since the hydrocarbons have lower surface tension, hydrocarbons on the surface increase the hydrophobicity of the surface. Thus, the contact angle of water on the treated surfaces increased with time after the treatment. Different substrates showed different tendency to be re-contaminated. The basic theory of "like dissolves like" can explain this phenomenon. BCB is the easiest to be re-contaminated. As was mentioned earlier, BCB is mainly composed of hydrophobic carbon-hydrogen rings, thus it has high affinity to the hydrocarbon contaminant in the air. Another possible reason for increase of contact angle of liquid on UV/O_3 treated surface with time after treatment is that low molecular weight species (absorbed from the environment or inherently contained in the substrate) diffuse from sub-surface to surface. BCB passivation is prepared by crosslinking low molecular weight species

TABLE IV
CHARACTERIZATION OF LIQUID UNDERFILL AND THE WETTING ON BCB

Underfill	γ (mJ/m^2)	θ (degree)	W_a (mJ/m^2)
No CA	39.1	24	74.8
CA-1	39.3	23	75.6
CA-2	39.1	16	76.7
CA-3	40.1	22	77.3
CA-4	35.7	19	69.4
CA-5	37.8	25	72.0
CA-6	38.5	27	72.8

TABLE V
CONTACT ANGLE (IN DEGREE) OF THREE LIQUIDS ON CURED UNDERFILL MATERIAL WITH AND WITHOUT COUPLING AGENT (CA)

underfill	H_2O	HOC_2H_4OH	CH_2I_2
No CA	83	54	36
With CA-1	85	56	39
With CA-2	73	59	36
With CA-3	66	49	35
With CA-4	81	66	50
With CA-5	80	53	34
With CA-6	77	54	34

into a highly crosslinked structure. Possibly, there is a very small amount of low-molecular-weight species in the BCB passivation, which may diffuse to the surface. During UV/O_3 treatment, this low molecular weight species on surface is removed. However, after UV/O_3 treatment, the low molecular weight species diffuse from the sub-surface onto surface.

Alumina is a pure inorganic material, it has hydrophilic hydroxyl groups on its surface. Thus, it has low affinity to the hydrocarbons and is not easily re-contaminated by hydrocarbon contaminant. In polyimide and FR-4 board, both of the base resins have hydrophilic polar groups as well as hydrophobic carbon-hydrogen moiety in their structures. They have higher affinity with hydrocarbon contaminant than inorganic alumina does, thus polyimide and FR-4 board showed faster re-contamination.

C. Work of Adhesion for Underfill with BCB

The underfill surface tension was determined by the pendant drop method (Table IV). The surface tension of the underfill materials was in the range of 35 to 40 mJ/m^2. There was no great difference among the underfills with different coupling agents. Underfill with coupling agent CA-4 showed the lowest surface tension. The contact angles of those underfill materials on BCB passivation were measured too, and they are also listed in Table IV. The contact angles of underfills on BCB were in the range of 15 to 27^o. Among them, the underfill with CA-6 had the highest contact angle; while the underfill with the addition of CA-2 had the lowest contact angle. From (6), the thermodynamic work of adhesion of the uncured underfill to BCB was calculated, and the results are also listed in Table IV. The work of adhesion of uncured underfill with BCB was in the range of 70 to 78 mJ/m^2. Among these samples, the underfill with coupling agent CA-4 showed the lowest thermodynamic work of adhesion with BCB passivation.

TABLE VI
SURFACE TENSION OF CURED UNDERFILLS AND THEIR THERMODYNAMIC WORK OF ADHESION WITH BCB

	γ (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^+ (mJ/m^2)	γ^- (mJ/m^2)	W_a (mJ/m^2)
No CA	42.14	41.75	0.01	3.88	71.64
CA-1	42.13	41.75	0.01	3.61	71.62
CA-2	45.22	41.28	0.26	14.90	73.65
CA-3	43.06	41.84	0.02	18.57	72.52
CA-4	36.25	34.11	0.11	10.41	66.26
CA-5	42.44	42.44	0.00	5.71	71.87
CA-6	43.20	42.35	0.02	8.99	72.61

The surface properties of the cured underfill were also characterized by measuring contact angles of the three standard liquids on the polished cured underfill surface. The contact angle data are listed in Table V. The contact angles of water on those surfaces are above 45^o, indicating that all of the underfills were hydrophobic. The surface tension and its three components of the cured underfill materials were calculated, and are listed in Table VI. The cured underfill with CA-4 also showed the lowest surface energy of 36.25 mJ/m^2. Compared with the surface tension of the uncured underfill, the surface tension of the cured underfill was slightly higher. The work of adhesion of these cured underfill to BCB was calculated from (3)–(5), and they are also listed in Table VI. There was no large difference among the data, except that the underfill with CA-4 showed relatively lower value than the others.

D. Effect of Surface Treatment on Adhesion

Two sets of BCB passivated silicon were used to prepare the die shear samples for adhesion strength test. The first set of BCB passivated dies were cleaned without further UV/ozone treatment, and the second set of BCB passivated dies were treated with UV/ozone after cleaning. The die shear test results are shown in Fig. 5. There are huge differences among the die shear strengths for the underfill materials with BCB without UV/O_3 treatment. The addition of coupling agent CA-1 did not improve the adhesion of the underfill with BCB passivation. While the addition of the other coupling agents such as CA-2, CA-3, CA-4, CA-5, and CA-6 led to increases in adhesion of the underfill with the BCB passivation. Comparing data in Fig. 5 with data in Tables IV and VI shows that the thermodynamic work of adhesion of either uncured underfill or cured underfill is not correlated with the die shear strength of the underfill material on the BCB passivation. The coupling agent can introduce chemical bond at the interface between the underfill and passivation, increasing the interfacial adhesion and die shear strength. The thermodynamic work of adhesion does not account for the very strong interaction such as chemical bonding at the interface, thus they are not suitable for prediction of adhesion with very strong interfacial interaction. It was reported, however, that some correlation was found between fracture toughness and the thermodynamic work of adhesion [13].

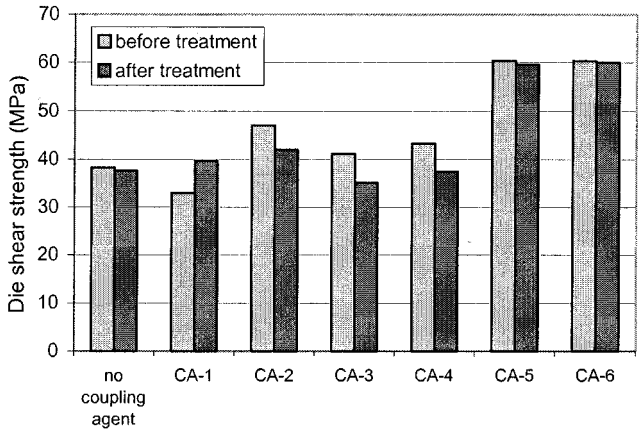

Fig. 5. Die shear strength of underfill with BCB passivation with and without UV/O_3 treatment.

TABLE VII
DIE SHEAR STRENGTH OF EPOXY UNDERFILL WITH UV/O_3 TREATED BCB

Time delay	Average (MPa)	Deviation (MPa)
No treatment	38.3	8.3
2 hours	37.8	10.5
3 minutes	37.3	10.8

TABLE VIII
DIE SHEAR STRENGTH OF UNDERFILL WITH ALUMINA

Underfill	Average (MPa)	Standard Deviation (MPa)
	Before treatment	
No CA	51.5	8.5
With CA-7	56.5	10.5
With CA-8	58.5	5.3
	After treatment	
No CA	60.1	9.0
With CA-7	62.0	9.0
With CA-8	66.8	8.0

The adhesion strengths of underfill with UV/O_3 treated BCB passivation are also shown in Fig. 5. In some cases, the UV/O_3 treated BCB showed slightly higher die shear strength (such as in the case of CA-1). In other cases, the UV/O_3 treated surface did not show higher die shear strength. Overall, there was no significant difference in die shear test results between UV/ozone treated BCB and untreated BCB.

The time delay between the UV/O_3 treatment and die shear sample preparation was not controlled for the set of die shear samples mentioned above. It ranged from 15 min to 2 h. Some die shear samples were prepared with UV/O_3 treated BCB passivated die with the time delay between surface treatment and die shear sample preparation controlled. One set of die shear samples were prepared 2 h after the UV/O_3 treatment. Another set of samples were prepared with the UV/O_3 treated BCB passivated silicon die in three minutes after the UV/O_3 treatment. The adhesion results are shown in Table VII. No significant difference showed up in the die shear strength among those samples. The surface treatment of BCB by UV/O_3 is not effective in improving its adhesion with an underfill.

Some small SiO_2 passivated dies and alumina boards were used to prepare die shear samples. During the die shear test, the interface between the underfill and alumina board failed. Thus, the die shear strength between the underfill and the alumina was obtained. The results are shown in Table VIII. The adhesion strength was slightly higher for all three formulations with UV/O_3 treated alumina than with untreated alumina. Thus, UV/O_3 treatment of alumina board can slightly improve the adhesion of alumina board with epoxy underfill.

IV. CONCLUSIONS

Surface tension of the substrates increased after UV/O_3 treatment, and the base component of the surface tension increased the most significantly. The large increase in base component of surface tension is probably due to the oxygen element, a Lewis base site, introduced during UV/O_3 treatment. Surface tension changes due to UV/O_3 treatment decayed with time after treatment. The change of surface tension of BCB after UV/O_3 treatment decayed the fastest, while it was slowest with treated alumina substrates. There was no correlation between thermodynamic work of adhesion and measured die shear strength. Surface treatment of BCB with UV/O_3 did not increase the adhesion strength significantly, while surface treatment of alumina substrate with UV/O_3 slightly improved the adhesion with epoxy underfill.

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REFERENCES

[1] J. C. W. van Vroonhoven, "Effects of adhesion and delamination on stress singularities in plastic-packaged integrated circuits," *J. Electron. Packag.*, vol. 115, pp. 28–32, 1993.

[2] C. K. Gurumurthy, J. Jiao, L. G. Norris, C. Y. Hui, and E. J. Kramer, "A new approach for thermal fatigue testing of the underfill/passivation interface," in *Application of Fracture Mechanics in Electronic Packaging,*. New York: ASME, 1997, vol. AMD-222/EEP-20, pp. 41–48.

[3] T. Y. Wu, Y. Tsukada, and W. T. Chen, "Materials and mechanics issues in flip-chip organic packaging," in *Proc. 46th IEEE Electron. Comp. Technol. Conf.*, 1996, p. 524.

[4] T. M. Moore and S. J. Kelsall, "The impact of delamination on stress-induced and contamination-related failure in surface mount ICs," in *Proc. 30 Int. Rel. Phys. Symp.*, San Diego, CA, March 30–April 2, 1992, pp. 169–176.

[5] L. T. Nguyen, A. S. Chen, and R. Y. Lo, "Interfacial integrity in electronic packaging," in *Application of Fracture Mechanics in Electronic Packaging and Materials*. New York: ASME, 1995, vol. 64, p. 35.

[6] R. van Gestel, K. de Zeeuw, L. van Gemert, and E. Bagerman, "Comparison of delamination effects between temperature cycling test and highly accelerated stress test in plastic-packaged devices," in *Proc. 30th Int. Rel Phys. Symp.*, San Diego, March 30–April 2, 1992, pp. 177–181.

[7] T. B. Lloyd, "Experimental procedures to characterize acid-base and dispersion force contributions to solid wettability," *Coll. Surf. A: Physicochem. Eng. Aspects*, vol. 93, pp. 25–37, 1994.

[8] R. J. Good and C. J. van Oss, "The modern theory of contact angles and the hydrogen bond components of surface energies," in *Modern Approach to Wettability: Theory and Applications*, M. E. Schrader and G. Loeb, Eds. New York: Plenum, 1992.
[9] R. J. Good, "Contact angle, wetting, and adhesion: a critical review," *J. Adhesion Tech.*, vol. 6, no. 12, pp. 1269–1302, 1992.
[10] R. K. Agrawal and L. T. Drzal, "Adhesion mechanisms of polyurethanes to glass surfaces," in *Proc. 8th Annu. Meeting Adhesives Soc.*, 1995, pp. 285–287.
[11] K. L. Mittal, Ed., *Contact Angle, Wettability, and Adhesion*. Utrecht, The Netherlands: VSP, 1992, ch. 1.
[12] K. L. Mittal and H. R. Anderson, *Acid-Base Interconnections: Relevance to Adhesion Science and Technology*. Utrecht, The Netherlands: VSP, 1991.
[13] H. R. Azimi, R. A. Pearson, and T. B. Lloyd, "Fundamentals of adhesion: The utility of three-liquid probe method," in *Proc. Applicat. Fracture Mech. Electron. Packag. Mater.*, 1995, p. 155.
[14] C. P. Wong and R. McBride, "Preencapsulation cleaning methods and control for microelectronics packaging," *IEEE Trans. Comp., Packag., Manufact. Technol. A*, vol. 17, pp. 542–552, Dec. 1994.

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